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Determination of Fiber Orientation of Cellulosic Samples by X-Ray Diffraction

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Synopsis

A method has been developed which permits the quantitative determination of fiber orientation in a cellulosic sample (paper, nonwoven or composite). From the measured fibril angle distribution function and the observed variation in intensity of the (002) plane of the x-ray pattern, a parameter governing the fiber distribution function is obtained analytically. The method is demonstrated for two different paper samples showing a narrow and a large fiber orientation distribution. The method is rapid for a series of samples involving the same fibers and does not involve any operator interpretation. It gives directly the average fiber orientation function from the bulk of the sample, not just from its surface as microscopic methods do. It can be particularly useful in the analysis of paper–polymer laminates.

INTRODUCTION

Most commercial papers are anisotropic as far as the orientation of the fibers is concerned. Since the mechanical properties depend upon the degree of orientation of the fibers, it is important to have rapid and accurate techniques to measure it.

A commonly used technique involves staining a small fraction of the fibers and the determination of their orientation by a microscopic method.[1–4] This is a tedious task which is time consuming due to the large number of fibers which must be considered in order to obtain a meaningful average and a complete distribution curve. In addition, the determination of the orientation of individual fibers is uncertain since most fibers are not straight.[1,2] The problem is further complicated by the "two-sideness" of the sheet: the wire and felt sides. This method therefore yields only the surface orientation of the paper.

Other methods such as x-ray diffraction,[5,6] light scattering,[7,8] and the zero-span test[9] have also been proposed. These proposals, however, are either qualitative in nature or of limited applicability. The present understanding of cellulose fiber morphology and paper structure suggests that the x-ray diffraction method can be used for a rapid, quantitative evaluation of the orientation distribution for cellulose fibers in a paper sheet or a cellulose composite. It is the purpose of the present paper to describe such a method.

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THEORY

Cellulose fibers are made up of four principal layers, termed the primary (P), outer secondary (S_1), middle secondary (S_2), and inner secondary (S_3) layers. Each secondary layer is made of crystalline cellulosic fibrils embedded in a lignin and hemicellulose matrix, and having a different fibrillar orientation. Since the majority of the cell wall material (80–95% depending upon the tree, growth season, and other variables) is contained in the S_2 layers, we will make the simplifying assumption that the x-ray fiber diagram can be analyzed by considering only this layer.

Since the (002) reflection is the most intense equatorial reflection in the fiber diagram of native cellulose, our analysis will be based uniquely on this particular reflection. In addition, we will assume that all fibers are collapsed and in the plane of the sample so that diffraction is due only to cell walls perpendicular to the x-ray beam (we will neglect the small amount of diffraction due to cell walls which are perpendicular to the plane of the sheet).

The diffraction geometry used is described in Figure 1. In a xyz coordinate system, the vector **P** normal to a diatropic (meredional) plane, e.g., (020), is defined by the angles α (or β) and ω. The incident x-ray beam is along the x-axis. For a cellulose fiber whose fiber axis is along z, any diatropic plane will produce on a flat plate film in the xz plane two symmetrical reflections made of two high-intensity regions located at azimuthal angles $\pm\Psi$ and $(180 \pm \Psi)$.

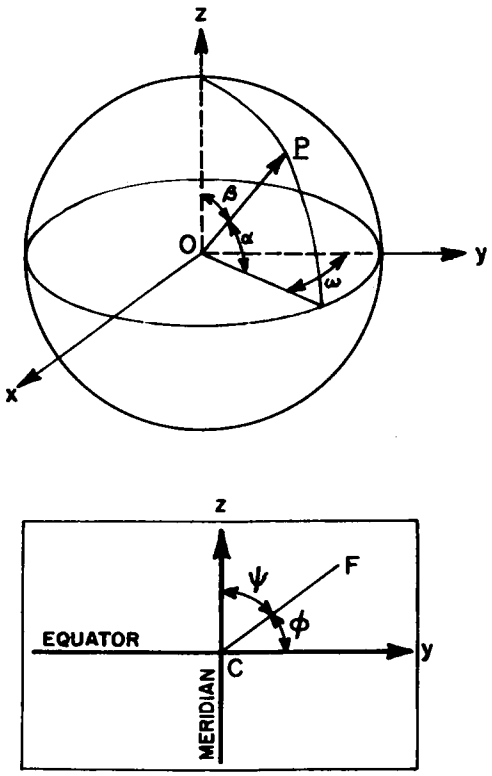

Fig. 1. Geometric representation of the x-ray diffraction system used.

The relationship between the position of **P** and the location of the diffracted intensity on the film when the fiber axis is perpendicular to the incident beam is given by the Polanyi relation[10]:

$$\sin \phi \cos \theta = \sin \alpha \tag{1}$$

where θ is the diffraction angle. This means that the distribution in orientation of the crystallites in the specimen is directly related to the intensity recorded on the x-ray photograph.

But if the vector **P** is normal to a paratropic (equatorial) plane, e.g., (002), instead of being normal to a diatropic plane as discussed before, then, in general, the intensity distribution of this plane on the photograph is no longer directly related to the orientation of the crystallites' main axes. It has been shown that two such paratropic reflections are needed to define exactly the fibrillar orientation.[11-14]

However, for fibers where no preferred orientation is present, one paratropic reflection suffices.[14] But the variation of intensity of the paratropic reflection chosen as a function of the angle ϕ is still not equal to the variation of intensity of the diatropic reflection as a function of the angle Ψ.[11-14]

For the model that we have chosen, when the two cell walls of the cellulose fiber are collapsed and in the yz plane ($\omega = 0$), the paratropic and diatropic variations of intensity are similar (this will be demonstrated experimentally in the next section), and one can write

$$I(\phi) = K_1 D(\beta) \tag{2}$$

and

$$\sin \phi \cos \theta = \sin \beta \tag{3}$$

where $I(\phi)$ is the x-ray intensity of the (002) reflection at an azimuthal angle ϕ; $D(\beta)$ is the number of (020) planes whose normal vectors **P** are oriented at an angle β with respect to the z axis; and K_1 is a proportionality constant. The angles β and ϕ, as shown experimentally,[15-17] are related through eq. (3).

At this point, we will start associating the fibril axis of the sample to the direction of **P**. This neglects the dispersion of crystallite orientation around the fibril axis, or fibril angle. Previous measurements have shown that this assumption is valid.[18] Thence, the function $D(\beta)$ can be called the fibril angle distribution function of the sample. For a single fiber having a fibril angle β_0, $D(\beta)$ is represented by two delta functions at angles $+\beta_0$ and $-\beta_0$, and this gives rise to a four-point diagram at angles $\pm\phi$, $\pm$ (180-ϕ) for the 002 plane.[15-17] For a paper sample, $D(\beta)$ is a broad function, often centered at zero degrees.[18,19]

Let us now consider a cellulosic sample where the individual fibers are oriented uniquely in the yz plane. If the ensemble of fibers is tilted away from the z direction by an angle ϵ, Figure 2, then eq. (2) becomes

$$I(\phi) = K_1 D(\beta - \epsilon) \tag{4}$$

But if there is distribution in orientation of the fibers, then one must write

$$I(\phi) = K_1 K_3 \int_\epsilon N(\epsilon) D(\beta - \epsilon) d\epsilon \tag{5}$$

where K_3 is a proportionality constant. The function $N(\epsilon)$ describes the ori-

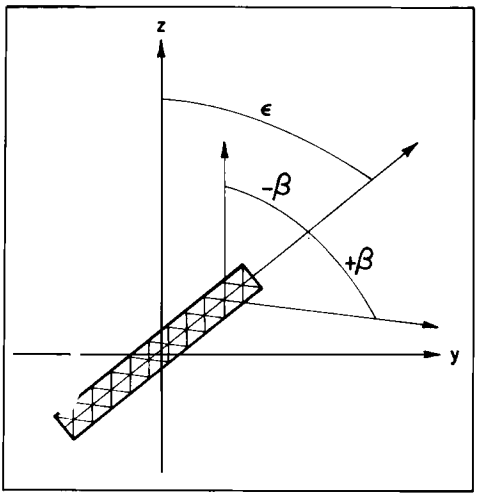

Fig. 2. Geometric representation of a fiber in the zy plane titled at an angle ϵ.

entation distribution of the fibers, which to a first approximation is assumed to be given by

$$N(\epsilon) = \frac{C}{C^2 \sin^2 \epsilon + \cos^2 \epsilon} \tag{6}$$

where C is an orientation parameter. When C is equal to unity, a random distribution is generated; when C is larger than unity, the fibers are preferentially aligned with respect to $\epsilon = 0$. The function $N(\epsilon)$ is given in Figure 3 for some values of C.

In this work, we are interested in the experimental determination of the function $N(\epsilon)$. Since the intensity function $I(\phi)$ is related through eq. (5) to two unknown functions, it is necessary to determine $D(\beta)$ by some independent technique. This can be done by using the reflectance method on the polarized microscope, as described by Page.[19] Once this function is known, it is possible to use a computer and to generate a series of curves corresponding to different orientation parameters C. This is illustrated in Figures 4 and 5 for a narrow and a broad fibril angle distribution function, respectively. The functions $D(\beta)$ are represented on these figures by the dotted lines. The theoretical functions $I(\phi)$ are presented, as a function of angle, for different values of the orientation parameter C. All the curves are arbitrarily normalized to unity at an angular value of zero, for comparison purposes. As expected, the dispersion in fiber orientation gives rise to a dispersion in the intensity curve. In addition, only a random distribution in fiber orientation ($C = 1.0$) gives a constant value of intensity. These curves indicate that the method is quite sensitive to fiber orientation since a significant change in the function $N(\epsilon)$ causes a significant change in the intensity function. Practically, one simply needs to superpose the experimental intensity curve to the corresponding theoretical curves, and to determine the orientation parameter C which best describes the sample. Then, the fiber oreintation distribution is read directly from Figure 3, or from eq. (6). This method will be more fully illustrated in the next sections using two paper specimens.

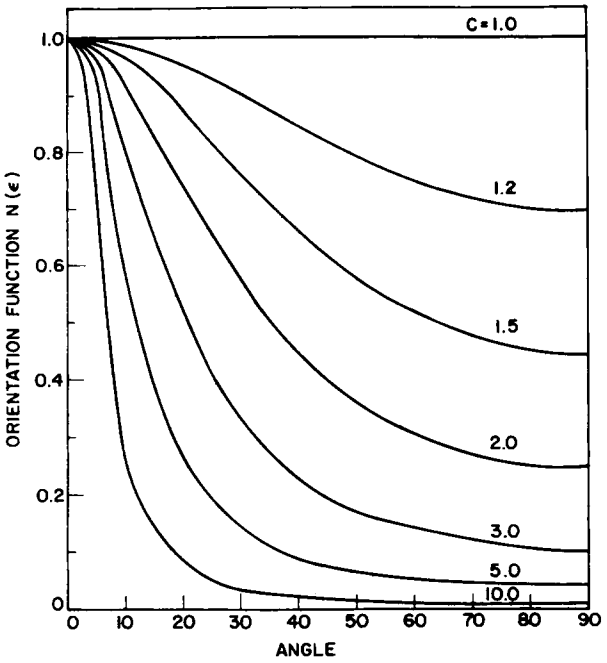

Fig. 3. Orientation function $N(\epsilon)$ plotted as a function of ϵ for different values of the orientation parameter C.

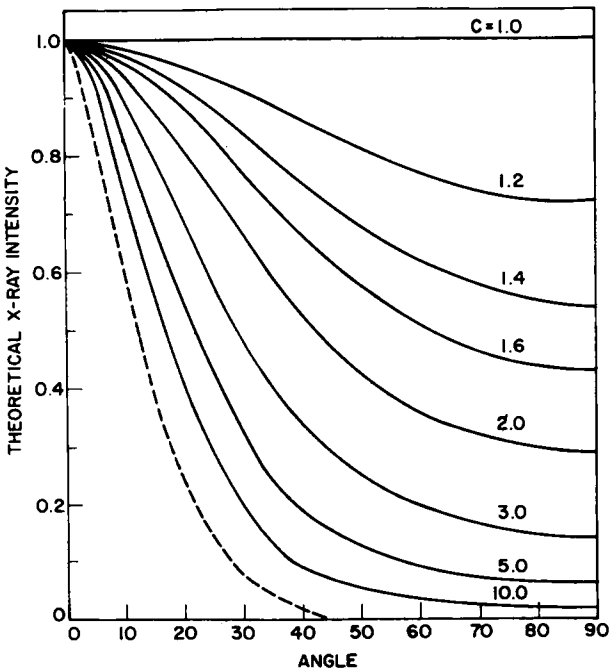

Fig. 4. Theoretical x-ray intensity curves computed for a narrow fibril angle distribution (dotted line) for different values of the orientation parameter C.

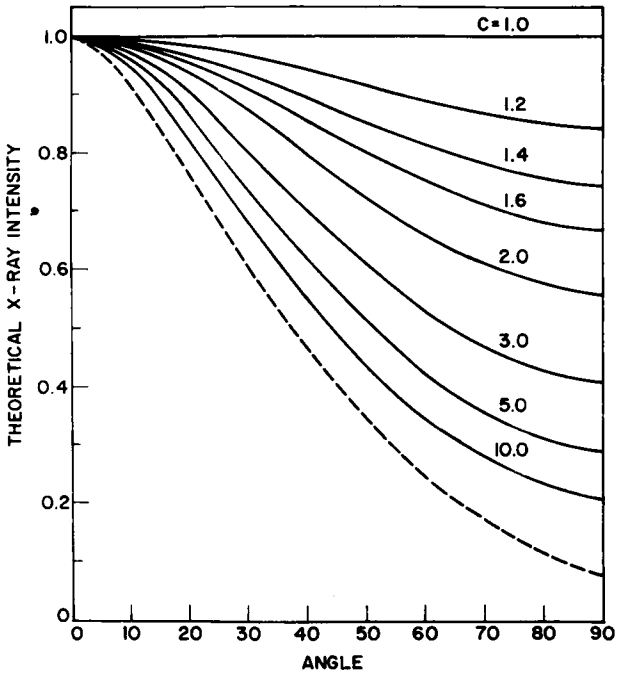

Fig. 5. Theoretical x-ray intensity curves computed for a broad fibril angle distribution (dotted line) for different values of the orientation parameter C.

EXPERIMENTAL

Measurements were made on two different sheets of paper, designated as PPO-92 and PPO-21. The sample PPO-21 was prepared from a commercial 56% yield Kraft pulp and made as an oriented sheet on a laboratory device.[20] The sample PPO-92 was prepared on the same machine and was made using a black spruce holocellulose pulp (56% yield). It was expected that the PPO-21 sample would consist of damaged fibers and would not show too much orientation. On the other hand, the PPO-92 fibers were expected to be undamaged and straight thereby yielding sheets with a high degree of orientation.

The mercury reflectance measurements were made following the technique described by Page.[19]

Photographic x-ray data were recorded using a CuK_α radiation with a modified Debye-Scherrer camera which could be evacuated. A collimator having a diameter of 0.025 in. was used. Photometric x-ray intensity scans were recorded on a Picker (FACS-1 system) x-ray diffractometer using CuK_α radiation. The instrument was controlled (PDP-8 minicomputer) by a program described by Desper.[21] The recorded values of intensity were corrected for background diffraction by a graphic technique involving radial scans of the intensity at various azimuthal angles. In the photometric method, the sample was always inclined towards the x-ray beam by the diffraction angle value θ, such that the Polanyi relations, eqs. (1) and (3), do not hold and that in eqs. (2), (4), and (5) the angles ϕ and β are equivalent.

The x-ray specimens were made from the superposition of four to eight layers (thickness of about 0.045 mm) chosen randomly in the paper sheet in order to obtain a representative surface area.

RESULTS AND DISCUSSION

Qualitatively, the preferred axial orientation of the fibers in the two samples can be seen on the corresponding x-ray photographs, Figure 6. Judging from the azimuthal intensity distribution of the equatorial reflections, sample PPO-92 is more oriented than PPO-21. For the sample PPO-92, the quantitative variation of intensity as a function of the azimuthal angle ϕ is presented in Figure 7 for the paratropic planes (002), (101), and (101), and for the diatropic plane (040) (as a function of $(90 - \phi)$). It can be seen that within the limits of experimental error, these four reflections have the same distribution of intensity as a function of angle, and consequently that none of these planes have any preferred orientation.[22] As stated before, this is a necessary condi-

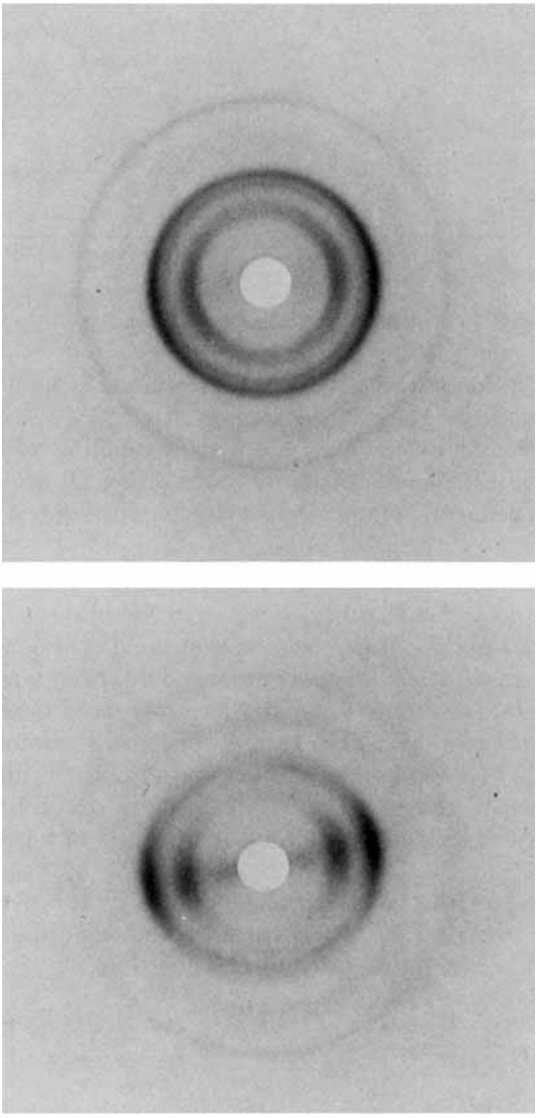

Fig. 6. X-Ray photographs obtained for the samples PPO-21 (top) and PPO-92 (bottom).

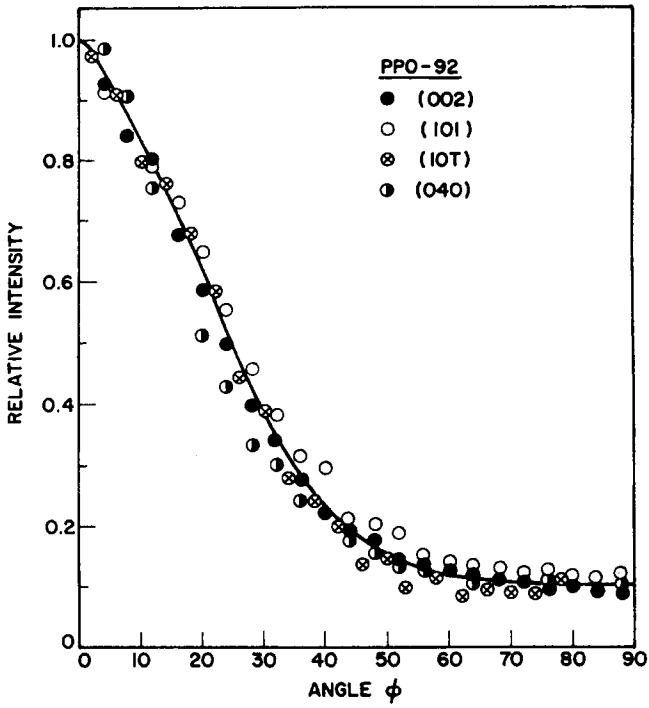

Fig. 7. Variation of x-ray intensity as a function of the angle ϕ for the sample PPO-92.

tion for the application of the method suggested in this paper. The same observations were made for the PPO-21 sample.

In order to determine the fiber orientation function of the sample, one needs to know the fibril angle distribution function $D(\beta)$. For the PPO-92 sample, it has been shown before[18] that it can be represented by

$$D(\beta) = \exp[-0.0157|\beta|^{1.5}]. \tag{7}$$

This function is plotted in Figure 8 along with the observed intensity distribution for the (002) plane. It can be seen that the dispersion in fiber orientation gives rise to an additional dispersion of the intensity curve. The experimental intensity data of Figure 8 can now be superposed to the theoretical results presented in Figure 4. This permits one to determine an orientation parameter of 4.4. The continuous line drawn in Figure 8 through the experimental data is the theoretical curve. It can be seen that the agreement is excellent, meaning that the distribution in fiber orientation is well represented by eq. (6).

For the sample PPO-21, the fibril angle distribution function is presented in Figure 9. This distribution is broader than the one obtained for the holocellulose pulp. It can be represented by the function

$$\left.\begin{aligned} D(\beta) &= \exp[-0.0099|\beta|^{1.5}] \quad \text{for } \beta \leq 40. \\ D(\beta) &= 0.0 \qquad\qquad\qquad\quad \text{for } \beta > 40. \end{aligned}\right\} \tag{8}$$

For the sample PPO-21, the fibril angle distribution function, eq. (8), and the variation of intensity of the (002) plane are presented in Figure 10.

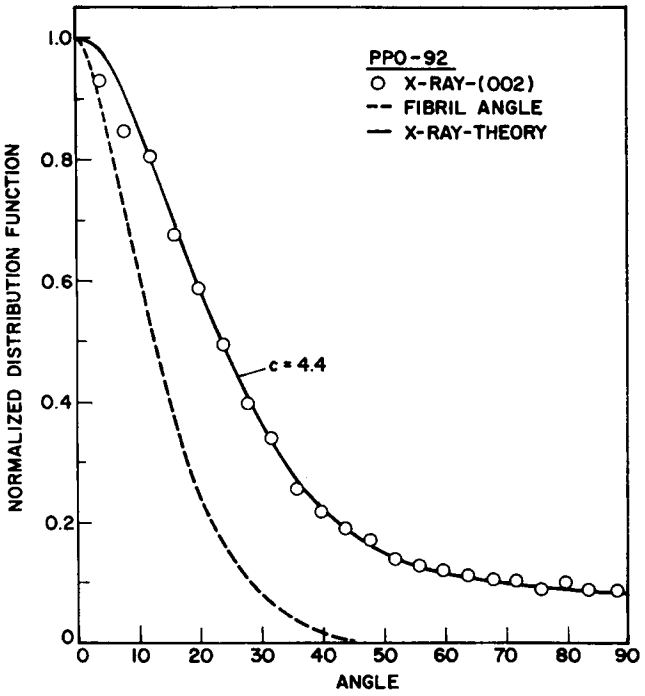

Fig. 8. Fibril angle distribution function and x-ray intensity distribution (experimental points) for the sample PPO-92. The continuous line through the experimental points is obtained theoretically considering an orientation parameter of 4.4.

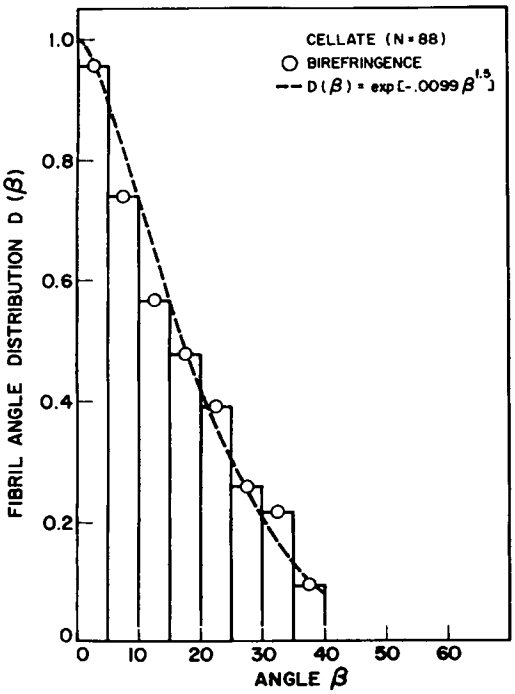

Fig. 9. Fibril angle distribution function $D(\beta)$ as a function of the angle β for the sample PPO-21.

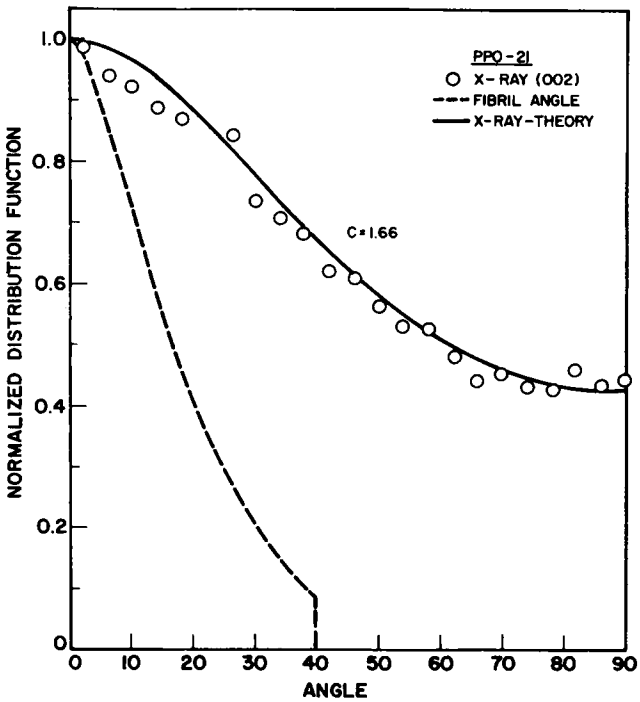

Fig. 10. Fibril angle distribution function and x-ray intensity distribution (experimental points) for the sample PPO-21. The continuous line through the experimental points is obtained theoretically considering an orientation parameter of 1.66.

Again, it is clear that the misorientation of the fibers induces some additional dispersion of the intensity data. One can now proceed as for the previous sample. Using the fibril angle distribution function, a graph similar to those presented in Figures 4 and 5 can be made assuming different orientation parameters for the function $N(\epsilon)$, eq. (6). This leads to the continuous line drawn in Figure 10 through the experimental data. Again the agreement is satisfactory when choosing an orientation parameter of 1.66. As expected, and as can be seen from Figure 3, the distribution in fiber orientation of this sample is broader than for the sample PPO-92.

Qualitatively, one can confirm the above conclusions by looking at the scanning electron micrographs presented in Figure 11. At the top, one sees the sample PPO-92, and at the bottom, the sample PPO-21, at two different magnifications. This indicates that in the sample PPO-92 the fibers are straight and rigid, and well oriented. In the sample PPO-21, the fibers are much more disoriented, and they are kinked and curved. On the other hand, in both cases, the fibers are well collapsed and flat; this justifies the assumption made in the theory.

CONCLUSIONS

A method is presented which allows one to determine quantitatively the distribution of fiber orientation of cellulosic samples from the measured fibril angle distribution function and the variation in x-ray intensity of the (002)

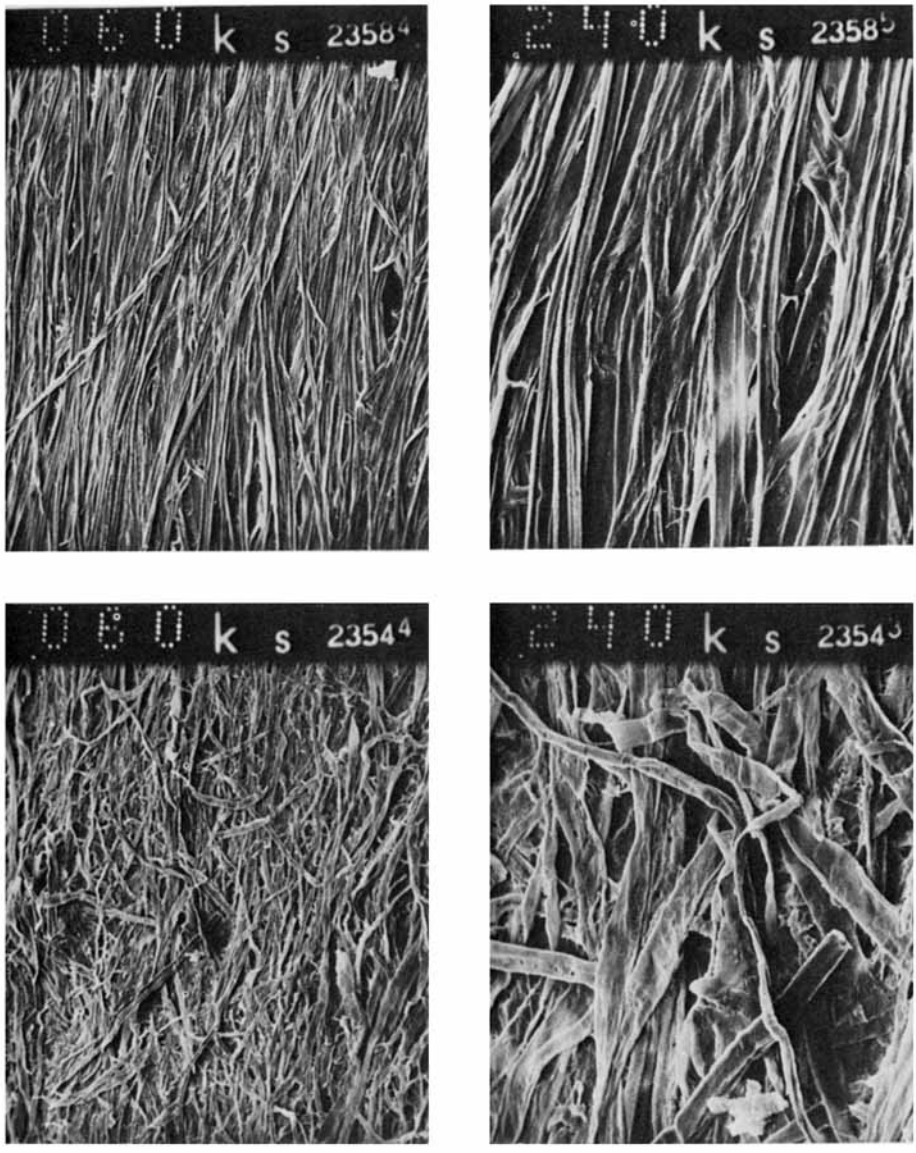

Fig. 11. Scanning electron photomicrographs for the samples PPO-92 (top) and PPO-21 (bottom) at two different magnifications.

plane. Important requirements are that the fibers be collapsed in the plane of the sample and that there be no preferred orientation of the (002) plane. These two assumptions have been justified for the two samples investigated. It is expected that they will hold for a large number of cellulosic samples (paper or composites).

One of the limitations of the method is that the fibril angle distribution function is required. This means that the analysis of a single sample is time consuming. However, this analysis gives two different distribution functions which are both related to the mechanical properties of the sample, while the staining method described earlier gives only one distribution function. On

the other hand, the x-ray analysis of a series of samples from a particular pulp can be made rapidly by this method since the fibril angle distribution needs to be done only once, and the x-ray intensity curve can be obtained very rapidly both photometrically or photographically. The method does not involve any operator interpretation and gives the average orientation of the whole sample, and not only from its surface.

In addition, the method can be used not only for sheets of paper, but also for the determination of fiber orientation in composites made by the lamination of one or several sheets of paper imbedded in thermoplastics. Several of these products are presently on the market. It is believed that only the method proposed in this paper can be used in these cases.

In all cases investigated in this paper, the fiber orientation function described by eq. (6) has been found satisfactory. But this function may not be applicable in all cases. If the agreement found by using eq. (6) is unsatisfactory, other functions have to be used.

The method can be alternatively used for determining the fibril angle distribution of the fibers in the sample. This can be done using eq. (5), but this requires that the fiber orientation distribution function $N(\epsilon)$ be determined by some other methods.

In this work, we have shown the validity of the x-ray diffraction method for the determination of fiber orientation of highly oriented specimens. There is no doubt that it can be used as well for less oriented samples, such as commerical papers.

References

1. R. Danielsen and B. Steenberg, *Svensk. Papperstidn.*, **50**, 301 (1947).
2. Z. C. Prusas, *Tappi*, **46**, 325 (1963).
3. O. L. Forgacs and I. Strelis, *Pulp and Paper Mag. Canada*, **64**, T-3 (1963).
4. G. Sauret, *Techniques et Recherches Papetières*, **Bull. No. 2**, 3, (1963).
5. G. Centola and D. Borruso, *Industria della Carta*, **9**, 95 (1955).
6. H. Ruck and H. Krässig, *Pulp and Paper Mag. Canada*, **59**, 183 (1958).
7. L. Rudström and U. Sjölin, *Svensk. Papperstidn.*, **73**, 117 (1970).
8. Y. W. Lim, A. Sarko, and R. H. Marchessault, *Tappi*, **53**, 2314 (1970).
9. O. J. Kallmes, *Tappi*, **52**, 482 (1969).
10. M. Polanyi, *Z. Phys.*, **7**, 149 (1921).
11. P. H. Hermans, *Physics and Chemistry of Cellulose Fibers*, Elsevier, Amsterdam, 1949.
12. P. H. Hermans, *Contribution to the Physics of Cellulose Fibers*, Elsevier, Amsterdam, 1946.
13. J. J. Hermans, appendix included at the end of reference 12.
14. J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger, *Rec. Trans. Chim.*, **65**, 427 (1946).
15. R. D. Preston, *The Molecular Architecture of Plant Cell Walls*, Chapman and Hall, New York, 1952.
16. K. E. Duckett and V. W. Tripp, *Text. Res. J.*, **37**, 517 (1967).
17. T. Radhakrishnan and N. B. Patil, *Text. Res. J.*, **38**, 209 (1968).
18. J. Noah and R. E. Prud'homme, submitted for publication.
19. D. H. Page, *J. Microsc.*, **90**, Pt. 2, 137 (1969).
20. A. A. Robertson and R. E. Prud'homme, in preparation.
21. C. R. Desper, Technical Report AMMRC TR 69-27, November 1969.
22. W. A. Sisson, *Ind. Eng. Chem.*, **27**, 51 (1935).

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